

Diffusion with restrictions

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Abstract

A non-linear diffusion equation is derived by taking into account hopping rates depending on the occupation of next neighbouring sites. There appears additional repulsive and attractive forces leading to a changed local mobility. The stationary and the time dependent behaviour of the system are studied based upon the master equation approach. Different to conventional diffusion it results a time dependent bump the position of which increases with time described by an anomalous diffusion exponent. The fractal dimension of this random walk is exclusively determined by the space dimension. The applicability of the model to describe glasses is discussed.

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There has been a lot of effort in understanding strongly interacting liquids, especially glass-forming, undercooled liquids^{1,2}. Obviously, the liquid-glass transition is primarily dynamic in origin characterized inevitably by a high cooperativity of local processes³. Due to the seminal papers of Götze et al⁴ and independently of Leutheuser⁵ the mode coupling theory for dense liquids offers a theoretical tool to study the slow dynamics in the vicinity of the glass transition. The mode coupling theory implies that the (ergodic) liquid state can be characterized by the decay of correlations whereas below a critical temperature T_c predicted by the approach it results a crossover to a solid-like behaviour where fluctuations are effectively frozen in. Furthermore, if additional thermal activated diffusion processes are taken into account the correlations decay but on a longer time scale⁶⁻⁸. The extended mode coupling theory^{9,10} leads to a more realistic behaviour of the correlation function.

The present paper is motivated by another kind of approach to supercooled liquids and glasses. It is based on a proposal due to Fredrickson-Andersen (FA)¹¹ to map the system onto an Ising model where the spin variables are related to local regions with a lower or a higher density than an averaged one. Such a facilitated model is analyzed above all numerically¹² but recently also analytically^{13,14}. Different to the conventional kinetic Ising model the dynamical rules for spin-flip processes are changed in order to take into account the enhanced immobility of the particles due to the gradual freezing with decreasing temperature. These restrictions can be easily formulated in a Fock space representation of the master equation by assuming flip rates which are dependent on the occupation of neighbouring sites promoting or preventing the processes under consideration. In this manner the inherent cooperativity manifested in a cooperative rearrangement of certain regions in order to change mobile states within the subsequent time steps into immobile ones and vice versa. The inclusion of mobile vacancies in the facilitated model^{15,16} yields to the occurrence of nearly nonactivated relaxation additional to the main α -process.

Here, we study another kind of secondary processes. They are due to the ability of the particles to diffuse when the system is above the so called glass temperature T_g . The diffusion constant goes to zero when the temperature is further decreased. Obviously, the mobility of the system is more and more reduced whenever the temperature reaches the glass temperature. Here, we consider diffusion for $T > T_g$ but take into account restrictions which lead to the above mentioned diminishing mobility. To this aim particles can jump from lattice site to lattice site which gives rise to diffusion on a large scale. To simulate the freezing process the hopping rate depends on the occupation of the nearest neighbour site of a given pair of sites between which a particle can jump. In such a manner the diffusion is more and more confined through the environment.

To describe this situation we use the mentioned Fock-space representation for the master equation under the influence of an exclusive dynamics. Such processes had been discussed in different contexts, compare for instance¹⁷⁻²². As already mentioned the starting point is the master equation which describes the stochastic process. A systematic approach is achieved by a mapping of the stochastic equation onto an evolution operator entering as the infinitesimal time evolution operator. This operator can be expressed in terms of second quantized operators. Physically it means the considered system is divided in small cells of size l (lattice points). Every cell is occupied by particles underlying dynamical rules depending on the situation in mind. From a quantum point of view two limiting cases can be realized, an unrestricted occupation number and a restricted one obeying the Pauli-principle with the

occupation numbers 0 and 1. This situation corresponds to a lattice gas representation with empty and single occupied sites which can be also interpreted as the two orientations within a spin model.

The case of unrestricted occupation had been discussed firstly by Doi²³ and had been further elaborated in^{19,24,25}. Here, we consider the case of a restricted occupation cell. Hence, the problem is to formulate the dynamics in such a way that this restriction is taken into account. The method offers a wide range of application, for a recent summary see²⁶.

The starting point is the Master equation which can be derived on quite general grounds. It can be written in the form

$$\partial_t P(\vec{n}, t) = L' P(\vec{n}, t) \quad (1)$$

where P is the probability that a certain configuration characterized by the vector \vec{n} at time t is realized. The evolution operator L' will be specified by the dynamics of the model. Following^{19,21,23–25} the probability distribution $P(\vec{n}, t)$ can be related to a state vector $|F(t)\rangle$ in a Fock-space according to $P(\vec{n}, t) = \langle \vec{n} | F(t) \rangle$ with the basisvectors $|\vec{n}\rangle$. As a consequence the Master equation (1) can be transformed to an equivalent equation in a Fock-space

$$\partial_t |F(t)\rangle = \hat{L} |F(t)\rangle \quad (2)$$

The operator L' in (1) is mapped onto the operator \hat{L} given in a second quantized form. Up to now the procedure is independent on the used operators. Usually \hat{L} is expressed in terms of creation and annihilation operators satisfying Bose commutation rules^{23–25}. To avoid double occupancy as for instance in a forest fire model²⁷ or a model simulating traffic jam²⁸ the method can be extended to the case of restricted occupation numbers per lattice sites,^{18–21} introducing Pauli-operators. These operators commute for different points and anticommute at the same lattice point. A further extension to a p-fold occupation has been discussed recently^{29,30}

The relation between the quantum formalism and the probability approach based upon the Master equation can be found by expanding the vector $|F(t)\rangle$ with respect to the basisvectors of the Fock-space

$$|F(t)\rangle = \sum_{\vec{n}} P(\vec{n}, t) |\vec{n}\rangle \quad (3)$$

As it was shown firstly by Doi²³ the average of an arbitrary physical quantity $B(\vec{n})$ is given by the average of the corresponding operator $\hat{B}(t)$

$$\langle \hat{B}(t) \rangle = \sum_{\vec{n}} P(\vec{n}, t) B(\vec{n}) = \langle s | \hat{B} | F(t) \rangle \quad (4)$$

This rule remains also valid as well as in case of Pauli-operators¹⁹ and parafermi-operators however with different meaning of the state vector $|s\rangle$ introduced in the last equation. Remark that the normalization condition for the state function is manifested in the relation $\langle s | F(t) \rangle = 1$ and the sum-vector $\langle s |$ can be expressed by $\langle s | = \sum_{\vec{n}} \langle \vec{n} |$. The evolution equation for an operator \hat{B} can be written

$$\partial_t \langle \hat{B} \rangle = \langle s | [\hat{B}, \hat{L}] | F(t) \rangle \quad (5)$$

To derive the last relation we have used $\langle s | \hat{L} = 0$. Note that dynamical equations of the classical problem are determined by the commutation rules of the underlying operators and the form of the evolution operator.

Now let us demonstrate the applicability of the method to describe diffusive motion under the influence of a constraint. In the second quantized formulation the hopping process is simply described by the evolution operator

$$\hat{L} = \sum_{\langle ij \rangle} J_{ij} (d_i^\dagger d_j - (1 - n_i) n_j) \quad (6)$$

where the hopping rate J_{ij} between the adjacent sites i and j can also depend on the occupation number of the next nearest sites, see below. Furthermore we have introduced the occupation number operator

$$n_i = d_i^\dagger d_i$$

Because the original problem is a classical one the operators d_i and d_i^\dagger satisfy the commutation rules for Pauli-operators. They commute at different lattice sites and anticommute at the same sites.

$$[d_i, d_j^\dagger] = \delta_{ij}(1 - 2n_i)$$

Using eq.(5) and the commutation relations we get the evolution equation for the averaged occupation number

$$\partial_t \langle n_r \rangle = \sum_{r(j)} \langle J_{rj} (n_j - n_r) \rangle \quad (7)$$

The evolution operator (6) allows diffusive processes between nearest neighbour sites whenever a double occupancy is avoided. Now let us generalize the model by including the above mentioned topological restrictions due to the freezing of the system. To this aim we have to include that the hopping rates J_{rj} depend on the occupation number n . As the simplest nontrivial assumption we chose

$$J_{rj} = J \sum_l \chi_{rjl} n_l \quad (8)$$

Here, χ_{rjl} is only nonzero when the triple of lattice indices rjl denotes nearest neighbours. Introducing the abbreviation $\Theta_{ij} = 1$ when i and j are nearest neighbours and zero otherwise one finds

$$\chi_{rjl} = \Theta_{rj} \Theta_{rl} (1 - \delta_{jl})$$

Let us visualize the processes for the one dimensional case. A particle can jump from site $i+1$ to the empty site i when the site $i-1$ is occupied. On the other hand a particle jumps from site i to the empty site $i+1$ under the condition that the site $i-1$ is occupied. In such a manner the hopping process is performed under the influence of attractive and repulsive forces as described before.

The kinetic equation for the averaged density reads

$$\partial_t \langle n_r \rangle = J \sum_{jl} \chi_{rjl} \langle n_j n_l - n_r n_l \rangle \quad (9)$$

There occurs a hierarchy of evolution equations which cannot be solved in general. Here the higher order terms are decoupled due to a mean field approximation. In the resulting equation we perform the continuum limit for the field $n(\vec{x}, t) = \langle n_i(t) \rangle$. The corresponding evolution equation is expanded upto the order of l^2 , where l is the cell size introduced before. The corresponding evolution equation in this order and in a low density expansion is written in the form

$$J^{-1} \partial_t n = (z - 1) n \nabla^2 n - 2(\nabla n)^2 \quad (10)$$

where z is the coordination number and for simplicity we have set $l = 1$. In case of a simple cubic lattice z is simply related to the space dimension via $z = 2d$. Because the hopping rate J_{ij} depends on the concentration itself the dynamical equation is not conserved.

The stationary solution $n_s(\vec{x})$ can be found from eq.(10)

$$|\nabla n_s(\vec{x})| = n_s(\vec{x})^{2/(z-1)} \quad (11)$$

For simplicity let us study a radial symmetric solution initiated by a radial symmetric initial condition. The exact result is

$$n_s(r) = \left[c_1 + c \frac{z-3}{(2-d)(z-1)} r^{2-d} \right]^{(z-1)/(z-3)} \quad (12)$$

where c and c_1 are constants. The special case $d = 2$ is incorporated since $(2-d)^{-1} r^{2-d}$ leads to a logarithmic term

$$n_s(r) = (c_1 + c \ln r)^3 \quad (13)$$

For large distances the solution behaves like

$$n_s(r) \simeq c r^{-\alpha} \quad \text{with} \quad \alpha = \frac{(z-4)(z-1)}{2(z-3)} = \frac{(d-2)(2d-1)}{2d-3} \quad (14)$$

where for $d = 2$ it results in $n_s \propto \ln^3 r$ which is different from conventional diffusion $n \propto \ln r$. Remark that the stationary solution in case of usual diffusion is described by an exponent $\alpha = d - 2$. Therefore $d = 2$ is a special case which will be also manifested in the dynamical analysis.

Now let us discuss the stability of the stationary solution against a time dependent perturbation. To this aim we write $n(\vec{x}, t) = n_s(\vec{x}) + n_1(\vec{x}, t)$. (From now on we include the coupling constant J introduced in eq. (8) in the time variable t .) It is easy to check that the correction term n_1 obeys

$$\partial_t n_1 = (z-1) (n_1 \nabla^2 n_s + n_s \nabla^2 n_1) - 4 \nabla n_s \nabla n_1 \quad (15)$$

Such a partial differential equation can be transformed into a diffusion like equation making the ansatz $n_1(\vec{x}, t) = \phi(\vec{x}) \psi(\vec{x}, t)$ where the function $\phi(\vec{x})$ is chosen in such a manner that the linear gradient term disappears:

$$(z-1) n_s \nabla \phi = 2 \phi \nabla n_s$$

As the result we find an equation where the contributions proportional to ψ cancel each other.

$$\begin{aligned} \partial_t \psi(\vec{x}, t) &= D(\vec{x}) \nabla^2 \psi(\vec{x}, t) \\ \text{with } D(\vec{x}) &= (z-1)n_s(\vec{x}) \end{aligned} \quad (16)$$

As before let us study a radial symmetric solution. Taking into account eq.(14) and inspecting the last equation in comparison with the diffusion equation we make the ansatz

$$\psi \propto t^{-\gamma} \exp\left(-b \frac{r^{\alpha+2}}{t}\right) \quad (17)$$

which allows to determine the unknown quantities γ and b :

$$\gamma = \frac{\alpha + d}{\alpha + 2} \quad \text{and} \quad b = \frac{1}{c(z-1)(\alpha+2)^2} \quad (18)$$

Like before the result leads to the conventional behaviour for $d = 2$. In the limit of an infinite range of the hopping process corresponding to $z \rightarrow \infty$ we find $\gamma = 2$.

Summarizing the results the radial symmetric solution of eq.(10) can be written for large distances r in scaling form

$$n(r, t) \simeq \frac{c}{r^\alpha} + t^{-\rho} f\left(\frac{r^{\alpha+2}}{t}\right) \quad (19)$$

where the exponents and the scaling function are given by

$$\rho = \frac{z-2}{\alpha+2} \quad f(v) = A v^{(2\alpha)/(\alpha+2)(z-1)} \exp(-bv) \quad (20)$$

To derive the last equation we have also used the radial symmetric solution of the function $\phi(r)$ introduced after eq.(15).

Inspecting eq.(19) one remarks that the dynamical part of the solution yields a maximum. The position of this bump r_b follows a simple law

$$r_b(t) \propto t^{\frac{1}{\alpha+2}} \quad (21)$$

Obviously, the bump is the more pronounced the lower the dimension. The result is depicted in Fig.1.

The exponent of diffusion d_w is simply defined by eq.(21)

$$d_w = \alpha + 2 \quad (22)$$

As mentioned the exponent agrees with that of conventional diffusion only in the two dimensional case. For instance for $d = 3$ it results $d_w = \frac{11}{3}$. We anticipate that d_w is considerably larger than 2 since many of the sites are already occupied due to the restriction introduced by eq.(8). As the consequence a lot of the neighbouring sites of a given pair of sites are unavailable to be reached by particles. Instead of that they are obliged to return to the starting point. The restrictions act like a cage for the particles. A similar conclusion can be drawn in case of a fractal lattice which leads also to an exponent d_w larger than two.

The position of the bump r_b moves much less rapidly with time t than for an unrestricted hopping.

In the next step we would like to discuss the influence of a heat bath with a temperature T . To this aim the Fock space formulation is extended by replacing the evolution operator \hat{L} by³¹

$$\hat{L} = \sum_{\langle ij \rangle} J_{ij} \left[(1 - d_i d_j^\dagger) \exp(-H/2T) d_i^\dagger d_j \exp(H/2T) \right] \quad (23)$$

where the Hamiltonian will be chosen to be

$$H = h \sum_r n_r + K \sum_{\langle r,s \rangle} n_r n_s \quad (24)$$

Here h means an external field (or chemical potential of the lattice gas) and K stands for the static coupling between nearest neighbours situated at the cells r and s . For $K > 0$ there is an additional repulsion whereas for $K < 0$ the particles are attractive. Remark that eq. (23) is in accordance with detailed balance.

Using the algebraic properties of Pauli-operators the evolution operator can be rewritten

$$\begin{aligned} \hat{L} &= \sum_{\langle ij \rangle} J_{ij} \left[(1 - d_i d_j^\dagger) d_i^\dagger d_j A_i B_j \right] \\ \text{with } A_i &= \exp \left(-K/T \sum_{s(i)} n_s \right) \quad \text{and} \quad B_i = A_i^{-1} \end{aligned} \quad (25)$$

The exact evolution equation for the density reads now

$$\begin{aligned} \partial_t \langle n_r \rangle &= \exp(K/T) \sum_{j(r)} \langle J_{rj} (U_r \nabla^2 V_j - V_r \nabla^2 U_j) \rangle \\ \text{with } U_r &= (1 - n_r) A_r \quad \text{and} \quad V_r = n_r B_r \end{aligned} \quad (26)$$

As far as the hopping parameter does not depend on the concentration itself the last equation can be represented as a continuity equation. However, in the case where the J_{ij} are determined by the concentration cf. eq.(8) the conservation law is not valid as already remarked in the non-thermalized approach. After performing the continuum limit we obtain in the one dimensional case

$$\partial_t n = n \partial_{xx} n - 2(\partial_x n)^2 + 4(K/T)(n \partial_{xx} n - (\partial_x n)^2 - n^2 \partial_{xx} n) \quad (27)$$

Applying the same procedure as before the last equation can be transformed in

$$\begin{aligned} \partial_t \psi &= \tilde{D}(x) \partial_{xx} \psi \\ \text{with } \tilde{D}(x) &= n_s(x) (1 + 4(K/T) n_s(x) (1 - n_s(x))) \end{aligned} \quad (28)$$

The only difference to eq.(16) is that $D(x)$ is replaced by $\tilde{D}(x)$. If $K > 0$, i.e. repulsive interaction, the modified diffusion function $\tilde{D}(x)$ is always positive and the general behaviour is only slightly changed. However if $K < 0$ (attraction) the quantity $\tilde{D}(x)$ can be negative

depending on the ratio $\frac{K}{T}$ and on the density n_s . A negative diffusion coefficient is obviously related to an instability.

In the present paper we have demonstrated that constraints during the diffusion process lead to a complete different behaviour. Due to the restrictions imposed on the diffusion process it appears a non-linear diffusion equation which can be analyzed partially in an analytical manner. There appears a maximum in the concentration which follows anomalous diffusion. Such a behaviour should be relevant for glassy materials characterized by rapid decrease of the mobility for decreasing temperatures. Further applications can be discussed when other degrees of freedom as impurities or vacancies are taken into account.

REFERENCES

- ¹ W. Götze, in *Liquids, Freezing and Glass Transition* edited by J. P. Hansen, D. Levesque and Zinn–Justin (North–Holland, Amsterdam); W. Götze and L. Sjögren, Rep. Prog. Phys. **55** (1992) 241.
- ² J. Jäckle, Rep. Prog. Phys. **49** (1986) 171.
- ³ G. Adams and J. H. Gibbs, J. Chem. Phys. **43** (1965) 139.
- ⁴ U. Bengtzelius, W. Götze, and A. Sjölander, J. Phys. C **17** (1984) 5915.
- ⁵ E. Leutheuser, Phys. Rev. A **29** (1984) 2765.
- ⁶ P. S. Das and G. F. Mazenko, Phys. Rev. A **34** (1986) 2265.
- ⁷ W. Götze and L. Sjögren, J. Phys. C **21** (1988) 3407.
- ⁸ L. Sjögren, Z. Phys. B **79** (1990) 5.
- ⁹ T. Franosch, W. Götze, M. R. Mayr, and A. P. Singh, Phys. Rev. E **55** (1997) 3183.
- ¹⁰ T. Franosch, M. Fuchs W. Götze, M. R. Mayr, and A. P. Singh, Phys. Rev. E **55** (1997) 7153.
- ¹¹ G. H. Fredrickson and H. C. Anderson, Phys. Rev. Lett. **53** (1984) 1244; J. Chem. Phys. **84** (1985) 5822.
- ¹² G. H. Fredrickson and S. A. Brewer, J. Chem. Phys. **84** (1986) 3351.
- ¹³ M. Schulz and S. Trimper, Int. J. Mod. Phys. B **24** (1997) 2927.
- ¹⁴ M. Schulz and S. Trimper, *Facilitated model for glasses*, submitted to Phys. Rev. B
- ¹⁵ M. Schulz and P. Reinecker, Phys. Rev. B **48** (1993) 9369.
- ¹⁶ C. Pigorsch, M. Schulz and S. Trimper, *An analytical approach to the modified Fredrickson–Anderson model*, submitted to Phys. Rev.
- ¹⁷ H. Spohn, *Large Scale Dynamics of Interacting Particles* (New York: Springer, 1991).
- ¹⁸ L. H. Gwa and H. Spohn, Phys. Rev. Lett **68** (1992) 725.
- ¹⁹ S. Sandow and S. Trimper, Europhys. Lett. **21** (1993) 799.
- ²⁰ G. Schütz and S. Sandow, Phys. Rev. E **49** (1994) 2726.
- ²¹ F. C. Alcaraz, M. Droz, M. Henkel and V. Rittenberg Ann.Phys.(N.Y.) **230** (1994) 250.
- ²² T. M. Ligget, *Interacting Particle Systems* (New York: Springer, 1985).
- ²³ M. Doi, J. Phys. A: Math. Gen. **9** (1976) 1465, 1479.
- ²⁴ P. Grassberger and M. Scheunert, Fortschr. Physik **28** (1980) 547.
- ²⁵ L. Peliti, J. Physique **46** (1985) 1469.
- ²⁶ R. B. Stinchcombe, Physica A **224** (1996) 248.
- ²⁷ H. Patzlaff and S. Trimper, Phys. Lett. A **176** (1994) 187
- ²⁸ M. Kaulke and S. Trimper, J. Phys. A: Math. Gen. **28** (1995) 5445
- ²⁹ M. Schulz and S. Trimper, Phys. Lett. A **216** (1996) 235.
- ³⁰ M. Schulz and S. Trimper, J. Phys. A: Math. Gen. **29** (1996) 6543
- ³¹ M. Schulz and S. Trimper, Phys. Rev. B **53** (1996) 8421.

FIGURES

FIG. 1. 3 dimensional plot $n(r, t)$ for $d = 1$